IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of
WADA et al.
Serial No. 10/618,638
For : LAMINATE FOR IR ABLATION

Group Art Unit 1773
Examiner Monique R. Jackson

TRANSLATOR'S DECLARATION

Honorable Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

I, Ritsuko Arimura, declare:

That I am well acquainted with both the Japanese and English languages;

That the attached document represents a true English translation of the certified copy of Japanese patent Application No. 207319/2002 filed on July 16, 2002; and

That I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 10th day of March, 2006.

Ritsuko Arimura

(Translation)

P A T E N T O F F I C E

J A P A N E S E G O V E R N M E N T

This is to certify that the annexed is a true copy of the following application as filed with this Office.

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Application Number : 207319/2002

Applicant(s) : Toyo Boseki Kabushiki Kaisha

Commissioner, Patent Office

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【List of the Annexed Documents】
【Document】 Specification One copy
【Document】 Drawing One copy
【Document】 Abstract One copy
【Proof】 Requested

【Document】 Specification

【Title of the Invention】 LAMINATE FOR IR ABLATION

【What is Claimed is】

【Claim 1】 A laminate for ablation comprising at least a substrate and an IR ablation layer, wherein the ablation layer comprises an IR absorbent metal layer.

【Claim 2】 The laminate for IR ablation of claim 1, which further comprises an IR non-sensitive polymer resin layer between the substrate and the IR absorbent metal layer.

【Claim 3】 The laminate for IR ablation of claim 1 or 2, wherein the IR absorbent metal layer is a metal deposition layer.

【Claim 4】 The laminate for IR ablation of claim 1, which comprises a release layer on an IR ablation layer on the opposite side from the substrate.

【Detailed Description of the Invention】

【0001】

【Technical Field to which the Invention pertains】

The present invention relates to a laminate for IR ablation used for producing a relief printing plate and a relief plate by computer plate making techniques.

【0002】

【Prior Art】

In the field of relief printing, flexo and the like, computer plate making techniques (computer to plate (CTP) technique), also known as digital image formation techniques, are becoming extremely general nowadays. In the CTP techniques, a photographic mask (also called a photomask or negative film) conventionally used for covering an area unwanted to be polymerized on a photosensitive printing plate has been replaced by a mask formed and integrated within the printing plate. There are two techniques in the market as a method to obtain such integrated mask. One is a method to

print a mask on a photosensitive plate by an inkjet printer, and the other is a method to form a mask by forming, on a photosensitive layer, a layer substantially non-transparent to ultraviolet rays (UV) (i.e., substantially blocks ultraviolet rays), and ablatable by irradiation of IR laser (this layer is generally referred to as an "IR ablation layer" etc. and is referred to as an "IR ablation layer" in the present specification), and forming an image on this layer with an IR laser. Using these techniques, an image (mask) is directly formed on a plate, and ultraviolet rays are irradiated through this image (mask) in the next step to afford plate making.

【0003】

The CTP technique is convenient in that it does not require a negative film and can afford a resolution far higher than that by a conventional technique using a negative film. A detailed discussion of the superiority of the CTP technique over the prior art is shown in, for example, "Deutsher Drucker, Nr. 21/3.6.99, pages w12-w16".

【0004】

In a photosensitive plate having the above-mentioned IR ablation layer, the IR ablation layer is generally made from a composition containing a polymer binder containing carbon black in a large amount. In general, a cover film is formed on an IR ablation layer for protection of the IR ablation layer during preservation of the plate and handling thereof, and this cover film is removed before irradiation of IR laser or after irradiation of IR laser (generally after main exposure and before development). However, printing cost becomes higher because carbon black in the IR ablation layer transfers to and stain a developer during developing with the developer after a main exposure (irradiation of ultraviolet rays) after IR ablation, which necessitates exchange of the developer each time a plate is made.

【0005】

Thus, there is a demand for a laminate for IR ablation, which solves the above-mentioned conventional problems, affords high grade printing images, reduces staining of developer, and which is applicable to various photosensitive resin layers.

【0006】

【Problems to be Solved by the Invention】

In view of the above-mentioned situation, it is therefore an object of the present invention to provide a laminate, which affords high grade printing images, reduces staining of developer, and which is applicable to various photosensitive resin layers, as compared to conventional laminates.

【0007】

【Means of Solving the Problems】

The present inventors have conducted intensive studies in an attempt to solve the aforementioned problems and completed the present invention. Accordingly, the present invention provides (1) a laminate for ablation comprising at least a substrate and an IR ablation layer, wherein the IR ablation layer comprises an IR absorbent metal layer, (2) the laminate for IR ablation of the aforementioned (1), which further comprises an IR non-sensitive polymer resin layer between the substrate and the IR absorbent metal layer, (3) the laminate for IR ablation of the aforementioned (1), wherein the IR absorbent metal layer is a metal deposition layer and (4) the laminate for IR ablation of the aforementioned (1), which comprises a release layer on an IR ablation layer on the opposite side from the substrate.

【0008】

【Mode of Embodiment of the Invention】

Fig. 1 is a sectional view of one embodiment of the laminate for IR ablation of the present invention, which comprises a substrate 1, an IR non-sensitive polymer resin

layer 2 and an IR absorbent metal layer 3, which is an IR ablation layer, and Fig. 2 is a sectional view showing one embodiment further comprising a release layer 4 laminated thereon. Fig. 3 shows application of the laminate for IR ablation of the present invention to a photosensitive resin plate, wherein the laminate for IR ablation of Fig. 1 is laminated as it is on the photosensitive resin layer 5, or the release layer 4 of the laminate for IR ablation as shown in Fig. 2 may be peeled off and the laminate for IR ablation is laminated on the photosensitive resin layer 5.

【0009】

In the present invention, the IR absorbent layer includes an IR absorbent metal layer, and by the "IR absorbent metal" is meant a metal, an alloy or a metal-containing compound capable of being ablated upon absorption of IR, wherein the alloy here includes not only a melt product of two or more kinds of metal elements but a melt product containing two or more kinds of metal elements as well as an element other than the metal elements. The "IR absorbent metal" may be one kind of material or a combination of two or more kinds of materials.

【0010】

Preferable examples of the above-mentioned metal include Al, Zn and Cu. Preferable examples of the above-mentioned alloy include an alloy of two or more kinds of metals selected from Ca, Sc, Tl, V, Sb, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ag, In, Sn, Ta, W, Au, Bi and Pb, and an alloy containing, along with the two or more kinds of metals, a non-metal element (carbon, silicon etc.) and/or a rare-earth element (Nd, Sm, Gd, Tb etc.). As the metal-containing compound, various compounds of metal oxide, metal nitride and the like can be used, as long as they absorb IR and are ablated. Of those, dark inorganic pigments such as copper chromite, chromic oxide, cobalt aluminate-chrome and the like are preferable.

For prevention of breakage and flaws (film strength) of the IR ablation layer, the IR absorbent metal is preferably a metal or an alloy, particularly preferably Al, Zn, Cu and a Bi-In-Cu alloy, particularly preferably Al.

【0011】

Examples of the material constituting the IR non-sensitive polymer resin layer in the present invention include polyamide, polyethylene, polypropylene, polyvinyl alcohol, polyacrylic acid, polyethylene oxide, amphoteric interpolymer, alkylcellulose, cellulose polymer (particularly hydroxypropyl cellulose, hydroxyethyl cellulose, nitrocellulose), copolymer of ethylene and vinyl acetate, cellulose acetate butyrate, polybutyral, cyclic rubber and the like. They may be used alone or in combination of two or more kinds thereof. The amphoteric interpolymer is described in US Patent No. 4,293,635.

【0012】

Of the materials exemplified above, polyvinyl alcohol, modified polyvinyl alcohol, polyacrylic acid, polyethylene oxide are used in the present invention in view of the developability in water or an aqueous medium, occurrence of wrinkles and the like. Of these, polyvinyl alcohol or modified polyvinyl alcohol having a degree of polymerization of 500 - 4000, preferably 1000 - 3000, and a degree of saponification of not less than 70%, preferably 80 - 99%, more preferably 80 - 90%, is used. As used herein, by the modified polyvinyl alcohol means one having carboxyl group, carbonyl group, polyoxyalkylene group, acetoacetyl group, sulfone group or silanol group introduced into a terminal or a main chain by secondary reaction with a compound reactive with hydroxyl group of polyvinyl alcohol (e.g., a compound having carboxyl group, double bond, aromatic ring and the like) or saponification of a copolymer of vinyl acetate and a different vinyl monomer.

【0013】

In the present invention, the IR ablation layer does not substantially allow transmission of ultraviolet rays (actinic radiation). That is, an optical density for actinic radiation exceeds 2.5, preferably over 3.5.

To meet the aforementioned optical density, the IR absorbent metal layer 3 preferably has a thickness of 70 - 20000 Å, more preferably 100 - 8000 Å, particularly preferably 100 - 5000 Å. When the thickness is less than 70 Å, masking function after IR ablation becomes unpreferably low, and when it exceeds 2000 Å, IR for image formation unpreferably fails to cause ablation.

【0014】

In contrast, when the IR ablation layer consists of the IR absorbent metal layer 3 and other IR absorbent material layer, the IR absorbent metal layer 3 preferably has a thickness of 50 - 15000 Å, more preferably 70 - 8000 Å, particularly preferably 100 - 5000 Å. When the thickness is less than 50 Å, masking function after IR ablation becomes unpreferably low, and when it exceeds 15000 Å, IR for image formation unpreferably fails to cause ablation.

【0015】

In the present invention, a release layer or a release film containing a release layer may be formed, and the release layer in the present invention is not particularly limited as long as it contains a releasable material. Particularly, a type containing a curable silicone resin is preferable. The release layer used in the present invention may be one containing a curable silicone resin, or one containing a curable silicone resin as a main component, or a modified silicone type produced by graft polymerization with an organic resin such as urethane resin, epoxy resin, alkyd resin and the like. As the curable silicone resin, any curing reaction type

such as addition type, condensation type, UV curable type, electron beam curable type, non-solvent type and the like can be used. Specific examples thereof include KS-774, KS-775, KS-778, KS-779H, KS-856, X-62-2422 and X-62-2461 manufactured by Shin-Etsu Chemical Co., Ltd., DKQ3-202, DKQ3-203, DKQ3-204, DKQ3-205 and DKQ3-210 manufactured by Dow Corning Asia, Ltd., YSR-3022, TPR-6700, TPR-6720 and, TPR-6721 manufactured by GE Toshiba Silicones Co., Ltd., SD7223, SD7226, SD7229 and LTC750A manufactured by Dow Corning Toray Silicone Co., Ltd. and the like. A release controlling agent and the like may be further added concurrently to control release property of the release layer.

【0016】

In the case of the aforementioned release film, a polyester film is preferable as a film, and as a method of laminating a release layer on the polyester film, conventionally known coating methods such as bar coating, reverse roll coating, gravure coating and the like can be used. The release layer may be laminated on one side of the polyester film, or may be laminated on both sides. When the release layer is laminated only on one side of the polyester film, an antistatic layer, an adhesive layer and the like may be laminated on the opposite surface side.

The thickness of the release layer is preferably 0.01-5 μm from the aspect of coatability. When the thickness of the release layer is less than 0.01 μm, stability tends to be insufficient in view of coatability, and a uniform coating film may be difficult to provide. On the other hand, when the thickness exceeds 5 μm, adhesion of the release layer itself to the coating film, curability and the like may be degraded.

【0017】

When the laminate for IR ablation of the present invention is applied to a photosensitive resin plate, the

laminates for IR ablation as shown in Fig. 1 may be directly laminated on a photosensitive resin layer 5, or the release layer 4 of the laminate for IR ablation as shown in Fig. 2 may be peeled off and the laminate for IR ablation may be laminated on the photosensitive resin layer 5.

The aforementioned photosensitive resin layer 5 is a layer made from a composition at least containing a known soluble synthetic polymer compound containing an elastomer binder and the like, a photopolymerizable unsaturated compound (in the following, to be also referred to as a crosslinking agent) and a photoinitiator. In addition, it may contain an additive, such as plasticizer, thermal polymerization inhibitor, dye, pigment, UV absorbent, flavoring and antioxidant.

【0018】

As the aforementioned soluble synthetic polymer compound, known soluble synthetic polymer compounds can be used. For example, polyetheramide (JP-A-55-79437 and the like), polyether esteramide (JP-A-58-113537 and the like), tertiary nitrogen-containing polyamide (JP-A-50-76055 and the like), ammonium salt type tertiary nitrogen atom-containing polyamide (JP-A-53-36555 and the like), addition polymer of amide compound having one or more amide bonds and organic diisocyanate compound (JP-A-58-140737 and the like), addition polymer of diamine without amide bond and organic diisocyanate compound (JP-A-4-97154 and the like) and the like are mentioned. Of these, tertiary nitrogen atom-containing polyamide and ammonium salt type tertiary nitrogen atom-containing polyamide are preferable.

【0019】

The elastomer binder may be a single polymer or a polymer mixture. It may be a hydrophobic polymer, a hydrophilic polymer or a mixture of a hydrophobic polymer and a hydrophilic polymer. Preferable examples of the hydrophobic polymer

include butadiene rubber, isoprene rubber, 1,2-polybutadiene, styrene-butadiene rubber, chloroprene rubber, nitrile-butadiene rubber, styrene-butadiene-styrene block copolymer, styrene-isoprene-styrene block copolymer, butyl rubber, ethylene-propylene rubber, chlorosulfonated polyethylene, butadiene-(meth)acrylic acid ester copolymer, acrylonitrile-(meth)acrylic acid ester copolymer, epichlorohydrin rubber, chlorinated polyethylene, silicone rubber and urethane rubber, which may be used alone or in combination of two or more kinds thereof. Preferable examples of the hydrophilic polymer include one having a hydrophilic group, such as -COOH, -COOM (M is monovalent, divalent or trivalent metal ion or substituted or non-substituted ammonium ion), -OH, $-NH_2$, $-SO_3H$, phosphoric acid ester group and the like, which is specifically polymers of (meth)acrylic acid or a salt thereof, copolymers of (meth)acrylic acid or a salt thereof and alkyl (meth)acrylate, copolymers of (meth)acrylic acid or a salt thereof and styrene, copolymers of (meth)acrylic acid or a salt thereof and vinyl acetate, copolymers of (meth)acrylic acid or a salt thereof and acrylonitrile, polyvinyl alcohol, carboxymethyl cellulose, polyacrylamide, hydroxyethyl cellulose, polyethylene oxide, polyethyleneimine, polyurethane having -COOM group, polyureaurethane having -COOM group, polyamic acid having -COOM group and salts thereof or derivatives thereof, which may be used alone or in combination of two or more kinds thereof.

【0020】

The photopolymerizable unsaturated compound preferably used above is exemplified by ring opening addition reaction product of polyglycidyl ether of polyhydric alcohol with methacrylic acid and acrylic acid. Examples of the aforementioned polyhydric alcohol include dipentaerythritol, pentaerythritol, trimethylolpropane, glycerine, ethylene glycol, diethylene glycol, triethylene glycol, ethylene oxide

adduct of phthalic acid and the like. Of these, trimethylolpropane is preferable.

【0021】

When the soluble synthetic polymer compound is an elastomer binder, preferable photopolymerizable unsaturated compound is a polymerizable ethylenically mono- or poly-unsaturated organic compound that can be used for the production of a photosensitive (polymerizable) printing plate and is compatible with elastomer binders. Examples of the compound include styrene, vinyltoluene, t-butylstyrene, α-methylstyrene, acrylonitrile, (meth)acrylic acid, methyl(meth)acrylate, ethyl(meth)acrylate, n-propyl(meth)acrylate, iso-propyl(meth)acrylate, n-butyl(meth)acrylate, iso-butyl(meth)acrylate, sec-butyl(meth)acrylate, t-butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, n-decyl(meth)acrylate, lauryl(meth)acrylate, n-tridecyl(meth)acrylate, stearyl(meth)acrylate, ethylene glycol mono(meth)acrylate, propylene glycol mono(meth)acrylate, diethylene glycol mono(meth)acrylate, dipropylene glycol mono(meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, polyethylene glycol monomethylether mono(meth)acrylate, polypropylene glycol monomethylether mono(meth)acrylate, polyethylene glycol monoethylether mono(meth)acrylate, polypropylene glycol monoethylether mono(meth)acrylate, n-butoxyethyl(meth)acrylate, phenoxyethyl(meth)acrylate, 2-phenoxypropyl(meth)acrylate, cyclohexyl(meth)acrylate, tetrahydrofurfuryl(meth)acrylate, glycidyl(meth)acrylate, allyl(meth)acrylate, benzyl(meth)acrylate, tribromophenyl(meth)acrylate, 2,3-dichloropropyl(meth)acrylate, 3-chloro-2-hydroxypropyl(meth)acrylate, N,N-diethylaminoethyl(meth)acrylate, N,N-

dimethylaminoethyl(meth)acrylate, N-t-butylaminoethyl(meth)acrylate, acrylamide, N,N-dimethylacrylamide, N,N-diethylacrylamide, ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, 1,3-butyleneglycol (meth)acrylate, 1,4-butanediol (meth)acrylate, neopentylglycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, 1,12-dodecanediol di(meth)acrylate, 1,14-tetradecanediol di(meth)acrylate, pentaerythritol di(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, glycelol di(meth)acrylate, glycelol allyloxy di(meth)acrylate, trimethylolethane di(meth)acrylate, trimethylolethane tri(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolpropane tri(meth)acrylate, dicyclopentyldimethylene di(meth)acrylate, dicyclopentadecane di(meth)acrylate, tricyclodecanediyldimethyl di(meth)acrylate, triallylcyanurate, triallylisocyanurate, triallyltrimellitate, diallylphthalate, divinylbenzene, polyurethane (meth)acrylate, polyester (meth)acrylate, oligobutadiene (meth)acrylate, oligoisoprene (meth)acrylate, oligopropylene (meth)acrylate and the like, which may be used alone or in combination of two or more kinds thereof.

【0022】

Preferable examples of the photoinitiator include benzophenones, benzoins, acetophenones, benzils, benzoin alkylethers, benzylalkylketals, anthraquinones, thioxanthones and the like, which are specifically benzophenone, chlorobenzophenone, benzoin, acetophenone, benzil, benzoin methylether, benzoin ethylether, benzoin isopropyl ether, benzoin isobutylether, benzyldimethylketal, benzyldiethylketal,

benzyldiisopropylketal, anthraquinone, 2-ethylanthraquinone, 2-methylanthraquinone, 2-allylanthraquinone, 2-chloroanthraquinone, thioxanthone, 2-chlorothioxanthone and the like, which may be used alone or in combination of two or more kinds thereof.

The photosensitive resin layer of the present invention may contain, besides soluble synthetic polymer compound, polymerizable compound and photoinitiator, additives such as plasticizer, heat polymerization inhibitor, dye, antioxidant and the like.

【0023】

The photosensitive resin layer can be prepared into a layer soluble or dispersible in a water-soluble developer, a semiwater-soluble developer and an organic solvent developer by appropriately changing the materials of each component. It is preferably made to be developable in water or an aqueous medium. When preparing a photosensitive resin layer that can be developed in water or an aqueous medium, it preferably corresponds to the photosensitive resin layer specifically described in EP-A767407, JP-A-60-211451, JP-A-2-175702, JP-A-4-3162, JP-A-2-305805, JP-A-3-228060, JP-A-10-339951 and the like.

【0024】

The substrate 1 of the present invention becomes a cover film when applied to a photosensitive resin plate, wherein the cover film is formed for the protection of the IR ablation layer during storage and handling of the plate, and removed (peeled off) before or after the IR irradiation.

【0025】

In the present invention, the substrate 1 preferably consists of materials of polyamide; polyvinyl alcohol; copolymer of ethylene and vinyl acetate; amphoteric interpolymer; cellulose polymers such as hydroxyalkylcellulose

and cellulose acetate; polybutyral; cyclic rubber and the like. As used herein, the amphoteric interpolymer is described in US Patent No. 4,293,635. These materials may be used alone or in combination of two or more kinds thereof. In addition, self-oxidative compounds such as nitrocellulose and nitroglycerine; non-self oxidative polymers such as alkylcellulose (e.g., ethylcellulose), polyacrylic acid and alkali metal salt thereof; polyacetal; polyimide; polycarbonate; polyester; polyalkylene such as polyethylene and polybutylene; polyphenylene ether; polyethylene oxide; polylactone; combinations thereof and the like can be also used.

【0026】

Besides the aforementioned, the material of the substrate (cover film) is preferably polyethylene, polypropylene, polyethylene terephthalate, polyethylene-2,6-naphthalate, nylon 6, nylon 4, nylon 66, nylon 12, polyvinyl chloride, polyvinylidene chloride, polyvinyl alcohol, full aromatic polyamide, polyamideimide, polyimide, polyetherimide, polysulfone, polyphenylene sulfide, polyphenylene oxide, and the like. Any of these may be used alone or two or more kinds thereof may be used in combination. In addition, a small amount of other organic polymer may be copolymerized or blended.

【0027】

The thickness of the support is preferably 10 - 300 μm, particularly preferably 10 - 200 μm.

【0028】

The support in the present invention is preferably a material having flexibility and superior in dimensional stability, and examples thereof include polyethylene terephthalate film, polyethylene naphthalate film, polybutylene terephthalate film, polycarbonate and the like. The support used here desirably has a thickness of 50 - 350 μm, preferably

100 - 250 μm, in view of mechanical property and shape stability of a plate and handling property during printing plate making and the like. Where necessary, a known adhesive conventionally used for this kind of purposes may be applied to improve adhesion between a support and a photosensitive resin layer.

【0029】

The method for producing the laminate for IR ablation of the present invention is not particularly limited. For example, the laminate can be obtained by forming an IR non-sensitive polymer resin layer on a substrate (cover film) by coating, spray coating and the like, and then successively forming an IR absorbent metal layer by vacuum deposition, sputtering and the like to form the other laminate.

【0030】

The method for preparing the aforementioned photosensitive plate is not particularly limited but generally, a photosensitive resin layer is formed on a support by applying, spray coating and the like to give one of the two laminates, or a protective film is peeled off from a commercially available photosensitive printing plate to give one laminate. Separately, the aforementioned laminate for IR ablation is formed, and these two laminates are laminated using a heat press machinery and the like. The laminating conditions are temperature: room temperature to 150°C, preferably 50 - 120°C, pressure: 20 - 200 kg-weight/cm^2, preferably 50 - 150 kg-weight/cm^2.

【0031】

A printing plate can be prepared from the aforementioned photosensitive resin plate as in the following.

After a cover film is or is not peeled off, an ablation layer is exposed to IR laser image for IR ablation, whereby a mask is formed on a photosensitive resin layer. Examples of

suitable IR laser include ND/YAG laser (1064 nm) and diode laser (e.g., 830 nm). A laser system suitable for a computer plate making technique is commercially available, and exemplified by diode laser system OmniSetter (registered trademark) (Fa. Misomex; laser wavelength: 830 nm; drum axis: 1800 mm) and ND/YAG laser system Digilas (registered trademark; Fa. Schepers). These include a rotary cylindrical drum to support a photosensitive plate, an IR laser irradiation apparatus and a layout computer. The image information is directly transmitted from the layout computer to the laser apparatus.

【0032】

After writing the mask on the IR ablation layer as mentioned above, the photosensitive plate is entirely exposed to actinic radiation through the mask. This is advantageously done directly on the laser cylinder. Alternatively, the plate may be removed from the laser apparatus and exposed to actinic radiation on a conventional flat irradiation unit. During the irradiation step, the photosensitive resin layer polymerizes in the area exposed in the above-mentioned mask forming step (ablation step) and otherwise in the IR ablation layer area which is covered with the IR ablation layer non-transparent to irradiation light. The actinic radiation may be applied in a conventional vacuum frame without oxygen, but it is advantageously applied in the presence of atmospheric oxygen.

【0033】

After exposure to actinic radiation as mentioned above, the plate is subjected to development. The development step can be performed using a conventional development unit, and depending on the properties of the plate, water, an organic solvent or a mixture thereof can be used. During the development, non-polymerized area of the photosensitive resin layer and the remaining part of the IR ablation layer are

removed. It is possible to first remove the IR ablation layer with one kind of a solvent or a solvent mixture and develop the photosensitive resin layer with a different developer. After the development step, the obtained printing plate is dried. The drying conditions of the plate are, for example, 45 - 80°C for 5 min - 4 hr. After drying, some post-treatments may be performed. For example, to make a printing plate non-adhesive, irradiation with a germicidal lamp or a treatment with Br_2 may be applied.

【0034】

【Examples】

In the following, the present invention is explained in detail by referring to Examples and Comparative Examples. The present invention is not limited by these examples.

Example 1

Preparation of ablation layer

An aqueous solution of polyvinyl alcohol (GOHSENOL AH-26 manufactured by NIPPON SYNTHETIC CHEMICAL INDUSTRY CO., LTD.)/propylene glycol (manufactured by ASAHI DENKA Co., Ltd.)/surfactant (EPAN 740 manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.)/pure water=8.75 g/8.75 g/0.01 g/332.5 g was applied to a PET film (whole cloth was manufactured by Toyo Boseki Kabushiki Kaisha, E5002, thickness 125 μm), that had undergone a chemical matte treatment, with a barcoater #26, and dried at 100°C for 3 min to form a film having a thickness after drying of 1 μm. Then, aluminum was evaporated on the surface of the film by vacuum deposition process in a thickness of about 800 Å. The optical density (OD) at this time was 3.5. The optical density (OD) was measured using a black and white transmission densitometer DM-520 (DAINIPPON SCREEN MFG. CO., LTD.).

【0035】

Reference Example 1

Preparation of plate

A PET protective film was peeled off from a photosensitive printing plate (Printight EF95GC, manufactured by Toyo Boseki Kabushiki Kaisha) consisting of a 250 μm thick PET film support (E5002, manufactured by Toyo Boseki Kabushiki Kaisha), a photosensitive resin layer, a polyvinyl alcohol layer and a PET protective film, and a polyvinyl alcohol layer thereunder was removed from the photosensitive resin layer with a conventional adhesive tape. The deposit surface of the aluminum deposited film prepared in the above-mentioned Example 1 was superimposed on the exposed photosensitive resin layer, and laminated using a heat press machine at 100°C, 100 kg-weight/cm^2 to give a plate consisting of a PET support, a photosensitive resin layer, an aluminum deposited layer, a polyvinyl alcohol layer and a chemical matte PET protective film (cover film). The total thickness of this plate was 1.05 mm.

【0036】

IR ablation

The chemical matte PET protective film (cover film) was peeled off from the above-mentioned plate. At this time, the protective film (cover film) alone was peeled off and the polyvinyl alcohol layer and the aluminum deposition layer remained on the photosensitive resin layer. This photosensitive resin layer was observed with a loupe (10× magnification). As a result, breakage and flaws were not observed in the polyvinyl alcohol layer and the aluminum deposition layer. This plate was wound around a rotary drum of Cyrel Digital Imager Spark (manufactured by BARCO) with the polyvinyl alcohol layer on the upper side and the support PET film on the back side. After vacuuming, an image was formed with diode laser. The laser output of this apparatus used was 4.8 mW, laser resolution was 2540 dpi, and laser spot diameter

was 15 μm. The rotary drum rotated at 1500 rpm. After IR ablation, the plate was taken out and observed with a loupe (10x magnification). As a result, aluminum deposition layer was ablated without any problem.

【0037】

Practicing plate making

The entire photosensitive printing plate covered with a digital image mask, which had undergone the above-mentioned IR ablation, was exposed to actinic radiation for 3 min and then developed at 25°C for 2 min with a conventional developing unit (TOMIFLEX; Washer manufactured by Tomihiro Sangyo). As a developer, used was tap water. During development, the remaining IR ablation layer (aluminum deposition layer, polyvinyl alcohol layer) and non-irradiated areas of the photosensitive resin layer were removed, leaving the area exposed to actinic radiation. After the development, the plate was dried at 70°C for 10 min and exposed to actinic radiation for 5 min.

The finished relief printing plate was examined with a loupe (10x magnification). All the test patterns of 2 point convex part and concave letters, 30 μm wide fine line, 100 μm diameter isolated dot and 156 lpi, 1% halftone dot were found to have been correctly formed.

【0038】

Example 2

Preparation for ablation layer

An aqueous solution of polyvinyl alcohol (GOHSENOL AH-26 manufactured by NIPPON SYNTHETIC CHEMICAL INDUSTRY CO., LTD.)/propylene glycol (manufactured by ASAHI DENKA Co., Ltd.)/surfactant (EPAN 740 manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.)/pure water=8.75 g/8.75 g/0.01 g/332.5 g was applied to a PET film (whole cloth was manufactured by Toyo Boseki Kabushiki Kaisha, E5002, thickness 125 μm), that had

undergone a chemical matte treatment with a barcoater #26, and dried at 100°C for 3 min to form a film having a thickness after drying of 1 μm. Then, aluminum was evaporated on the surface of the film by vacuum deposition process in a thickness of about 500 μm to form an IR ablation layer (IR absorbent metal layer). The optical density of the IR ablation layer was 3.5. The optical density (OD) is measured using a black and white transmission densitometer DM-520 (DAINIPPON SCREEN MFG. CO., LTD.).

【0039】

Reference Example 2

Preparation of plate

In the same manner as in Reference Example 1, a chemical matte PET protective film was released from a photosensitive flexo printing plate (Cosmolight NEO, manufactured by Toyo Boseki Kabushiki Kaisha) consisting of a 100 μm thick PET film support (E5002, manufactured by Toyo Boseki Kabushiki Kaisha), a photosensitive resin layer, a polyvinyl alcohol layer and a chemical matte PET protective film, and a polyvinyl alcohol layer thereunder was removed from the photosensitive resin layer using a conventional adhesive tape. The deposit surface of the aluminum deposited film prepared in the above-mentioned Example 2 was superimposed on the exposed photosensitive resin layer, and laminated using a heat press machine at 100°C, 100 kg-weight/cm^2 to give a plate consisting of a PET support, a photosensitive resin layer, an aluminum deposit layer, a polyvinyl alcohol layer and a chemical matte PET protective film (cover film). The total thickness of this plate was 1.90 mm.

【0040】

IR ablation

First, for back exposure to make the relief depth a generally employed depth of about 0.8 mm, the PET support side

of the above-mentioned flexo plate was exposed to actinic radiation (light source: Philips 10R, illuminance at 365 nm: 7.5 mW/cm^2) for 20 sec, and the biaxially stretched PET protective film (cover film) was peeled off. At this time, the protective film (cover film) alone was peeled off and the polyvinyl alcohol layer and the aluminum deposition layer remained on the photosensitive resin layer. This photosensitive resin layer was observed with a loupe (10x magnification). As a result, breakage and flaws were not observed in the polyvinyl alcohol layer and the aluminum deposition layer. This plate was wound around a rotary drum of Cyrel Digital Imager Spark (manufactured by BARCO) with the polyvinyl alcohol layer on the upper side and the support PET film on the back side. After vacuuming, an image was formed with diode laser. The laser output of this apparatus used was 4.8 mW, laser resolution was 2540 dpi, and laser spot diameter was 15 μm. The rotary drum rotated at 1500 rpm. After IR ablation, the plate was taken out and observed with a loupe (10x magnification). As a result, aluminum deposition layer was ablated without any problem.

【0041】

Practicing plate making

The entire photosensitive flexo printing plate covered with a digital image mask, which had undergone the above-mentioned IR ablation, was exposed to actinic radiation for 15 min and then developed at 40°C for 6 min with a developing machine (Stuck System) manufactured by Anderson & Vreeland, Inc. As a developer, used was tap water added with a 1% dishwashing detergent Cascade (manufactured by US Procter & Gamble Company). During development, the remaining IR ablation layer (aluminum deposition layer, polyvinyl alcohol layer) and non-irradiated areas of the photosensitive resin layer were removed, leaving the area exposed to actinic radiation. After

the development, it was dried at 60°C for 20 min, exposed to actinic radiation for 5 min and finally exposed to a germicidal lamp for 5 min to remove surface adhesiveness. Then, in the same manner as in Example 1, the entire surface of the plate was exposed to actinic radiation and developed to give a finished flexo printing plate, which was examined with a loupe (10x magnification). All the test patterns of 2 point convex part and concave letters, 30 μm wide fine line, 100 μm diameter isolated dot and 156 lpi, 1% halftone dot were found to have been correctly formed.

【0042】

Example 3

Preparation of ablation layer

A commercially available aluminum deposited CPP film (Chemirite S manufactured by NAKAI KOGYO CO., LTD., film thickness 25 μm, thickness of aluminum deposition 750 Å) was used.

※ CPP film: unoriented polypropylene film

【0043】

Reference Example 3

Preparation of plate

In the same manner as in Reference Example 1, a photosensitive resin layer of a photosensitive printing plate (Printight EF95GC manufactured by Toyo Boseki Kabushiki Kaisha) was exposed and the deposit surface of the aluminum deposited film was superimposed on the exposed photosensitive resin layer and laminated using a heat press machine at 80°C, 100 kg-weight/cm^2, whereby a plate comprising a PET support, a photosensitive resin layer, an aluminum deposition layer and a CPP film was obtained. The total thickness of this plate was 0.98 mm.

【0044】

The CPP film (cover film) of the plate prepared above was

peeled off. As a result, only the CPP film (cover film) was peeled off and the aluminum deposited layer remained on the photosensitive resin layer. In addition, the surface of the photosensitive resin layer was observed with a loupe (10x magnification) to find no breakage or scratches on the aluminum deposited layer. In the same manner as in Reference Example 1, images were formed (IR ablation) on the plate after back exposure using a diode laser, and the plate was taken out and observed with a loupe (10x magnification). As a result, no problem was found and ablation of an aluminum deposition layer was confirmed.

Thereafter, in the same manner as in Reference Example 1, the entire surface of the plate was exposed to actinic radiation, developed, and the resulting relief printing plate was checked with a loupe (10x magnification). As a result, all test patterns of 2 point convex part and concave letter, 30 μm wide fine line, 100 μm diameter isolated dot and 156 lpi, 1% halftone were found to have been accurately formed.

【0045】

Comparative Example 1

Using the components shown in the following Table 1, a dispersion containing carbon black, polyvinyl alcohol (GOHSENOL GH-23, manufactured by NIPPON SYNTHETIC CHEMICAL INDUSTRY CO., LTD., thermal decomposition starting temperature: 220°C, Limited Oxygen Index: 22.5) and a plasticizer was prepared. This dispersion was applied onto a PET film (thickness 125 μm) with a #26 barcoater and dried at 100°C for 3 min to evaporate water, whereby smooth non-adhesive coating film (coated amount 4.1 g/m^2 and optical density of actinic radiation area 4.8) was obtained, or a laminate for ablation, which comprised an IR ablation layer and a PET film.

【0046】

【Table 1】

Component	Amount added (g)	Weight without water (%)	Note
3% aqueous solution of GH-23	53.9	36.3	
polyethylene glycol #400	1.13	25.4	plasticizer
EPAN 740	0.004	0.09	dispersant (surfactant)
carbon black CW1	8.5	38.2	20% aqueous dispersion
distilled water	36.0	-	

carbon black CW1: manufactured by Orient Chemical Industries, Ltd.
polyethylene glycol #400: manufactured by Nacalai Tesque, Inc.
EPAN 740: manufactured by Dai-ich Kogyo Seiyaku Co., Ltd.

【0047】

Reference Example 5

Preparation of plate

The PET film (cover film) having an IR ablation layer, which was prepared in the above-mentioned Comparative Example 1, and a photosensitive printing plate as used in Reference Example 1 were laminated using a heat press machine at about 100°C, 100 kg-weight/cm^2 to give a plate comprising a PET support, a photosensitive resin layer, an IR ablation layer and a PET film (cover film).

Then, the PET film, which was a cover film of the obtained plate, was peeled off, and in the same manner as in Reference Example 1, the IR ablation layer was examined upon enlargement with a loupe (10x magnification) before exposure to actinic radiation. As a result, partial breakage and numerous flaws were found.

In the same manner as in Reference Example 1, the plate was developed after exposure to actinic radiation. As a result, the developer was stained with a large amount of carbon black, and the developer could not be used for the production of the next plate. The finished flexo printing plate was examined with a loupe (10x magnification). As a result, small convex parts and defective parts of the relief other than the

desired image were found due to the effect of flaws occurred on the aforementioned IR ablation layer, and image reproducibility was poor.

【0048】

【Effect of the Invention】

As is clear from the foregoing explanation, by using the laminate for IR ablation of the present invention, conventional facility and method can be used as they are, easy and high-precision formation of a mask is possible, and a printing plate and a relief plate that afford high grade printed images can be obtained. In addition, the developer does not get very dirty during developing and plural sheets can be developed continuously, and the like, and the present invention greatly contributes to industry.

【Brief Description of the Drawing】

Fig. 1 is a schematic sectional view showing a first embodiment of the laminate for IR ablation of the present invention.

Fig. 2 is a schematic sectional view showing one embodiment of the laminate for IR ablation of the present invention further comprising a release layer.

Fig. 3 is a schematic sectional view wherein the laminate for IR ablation of the present invention is applied to a photosensitive resin plate.

【Explanation of the Symbols】

1 substrate

2 IR non-sensitive polymer resin layer

3 IR absorbent metal layer (IR ablation layer)

4 release layer (release film)

5 photosensitive resin layer

6 support

【Document】 Abstract

【Summary】

【Problem】 Provision of a laminate, which affords high grade printing images, reduces staining of developer, and which is applicable to various photosensitive resin layers.

【Solving Means】 (1) A laminate for ablation comprising at least a substrate and an IR ablation layer, wherein the IR ablation layer comprises an IR absorbent metal layer, (2) the laminate for IR ablation of the aforementioned (1), which further comprises an IR non-sensitive polymer resin layer between the substrate and the IR absorbent metal layer, (3) the laminate for IR -ablation of the aforementioned (1), wherein the IR absorbent metal layer is a metal deposition layer and (4) the laminate for IR ablation of the aforementioned (1), which comprises a release layer on an IR ablation layer on the opposite side from the substrate.

【Main Drawing】 Fig. 1

FIG. 1

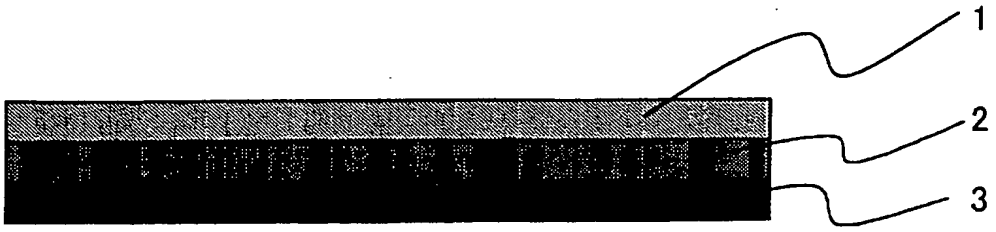

FIG. 2

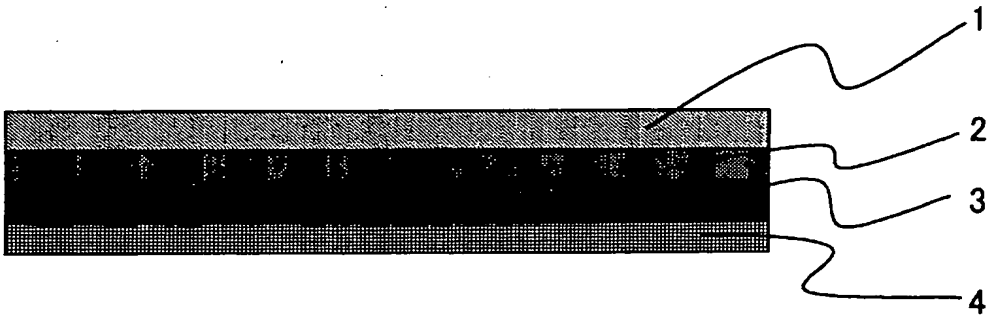

FIG. 3